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(54) COATING OF GLASS SURFACES

(71) We, SAINT-GOBAIN INDUSTRIES, a Body Corporate organised under the laws of the French Republic, of 62 Boulevard Victor Hugo, 92209 Neuilly Sur Seine, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of making glass articles, including flat glass sheets, coated with a film comprising titanium oxide.

It is known that flat glass covered with a film of metal oxide may be obtained by depositing on the glass heated to an elevated temperature a solution of metal acetyl acetonates to form a film of metal oxide of warm colour, the film being formed of a mixture of oxides chosen from cobalt oxide, chromium oxide and similar oxides.

On the other hand there is also used a film of titanium oxide as a coloured coating of cold colour on flat glass, this film being obtained by atomising a solution of titanium acetyl acetonate on the glass heated to a high temperature. However the film of titanium oxide prepared by this method has the disadvantage of not being uniform when the film is too thin or too thick. In particular in the case of a thick film the inequalities in thickness may be visible to the naked eye and the film is often formed of irregular depositions. On the other hand the mechanical properties and chemical intertness of the film leave something to be desired.

The above mentioned faults render the flat glass obtained unsaleable as a heat reflecting pane.

It has been found that the characteristics of thermal decomposition of the titanium chelates depend on the inertness of the compound to hydrolysis. Titanium acetyl acetonate, which has a high rate of hydrolysis, is decomposed at a relatively low temperature in comparison with other titanium compounds having a low rate of hydrolysis.

On the other hand the rate of thermal decomposition of titanium acetylacetonate is influenced only slightly by the temperature of the glass on which the solution is deposited and the effectiveness of the deposition on the glass to obtain a film of titanium oxide is very high, but the film obtained is not uniform and has mediocre mechanical properties and chemical intertness. Other experiments have shown that titanium tetraoctylene glycol and titanium triethanolamine, which are subject to hydrolysis at a much lower speed than other chelate compounds of titanium, have the disadvantage that the compounds are strongly influenced by the temperature of the glass regarding their efficiency of deposition in the form of titanium oxide. However these compounds provide extremely uniform films on the glass. Other experiments have also shown that titanium methyl acetoacetate and titanium ethylacetoacetate, of which the speeds of hydrolysis are intermediate between that of titanium acetyl acetonate and titanium tetraoctylene glycol and titanium triethanolamine, have intermediate values regarding the efficiency of deposition on the glass as well as a good film uniformity. From these results the applicant has developed a method allowing elimination of the above mentioned disadvantages of titanium oxide films obtained from titanium acetylacetonate.

According to the invention there is provided a method of applying a coating comprising titanium oxide to a glass surface, in which a solution containing at least two titanium compounds selected from titanium acetylacetonate, titanium methyl acetoacetate, titanium ethyl acetoacetate, titanium tetraoctylene glycol and titanium triethanolamine is applied to the surface which is at an elevated temperature sufficient to decompose the compounds to titanium oxide.

The solution preferably comprises an organic solvent having a boiling point of at least 100°C and capable of dissolving said titanium chelates.

The process of the invention may be applied to flat glass, glass bottles and other articles of glass. It may also be used in an effective manner on a ribbon of glass which is manufactured continuously starting from molten glass.

To deposit the solution of titanium compounds it is preferable to operate by atomising said solution onto the glass heated to a high temperature. It is also preferable in the present invention to pre-heat the flat glass to a high temperature and to maintain it at a temperature slightly lower until there is obtained on the glass a film of the desired thickness.

Taking account of the deformation temperature of the glass it is advisable to choose temperatures from 500 to 700°C.

In the present invention it is possible to add to the solution containing titanium chelates, a metallic compound which is thermally decomposable to give a coloured metallic oxide, such as cobalt oxide, iron oxide, nickel oxide or chromium oxide, but it is usually preferable to use a solution containing only the chelate compounds of titanium when a layer containing titanium oxide only is desired.

In the use of the invention the solution of titanium compounds is prepared by adding to a solvent at least two compounds chosen among the five chelates of titanium mentioned above, the optimum composition of the solution being a function of the operating conditions. The most advantageous composition may be chosen as a function of the glass temperature, its thermal capacity and the desired thickness of the film. For example when the temperature of the glass is relatively high and its thermal capacity is relatively large the use of a relatively large quantity of titanium tetraoctyleneglycol and/or titanium triethanolamine (which have a decomposition temperature which is relatively high) provides a film which is very strong and has an excellent uniformity. When the temperature of the glass is relatively low and its thermal capacity is relatively small it is preferable to use a relatively large quantity of titanium acetylacetonate (which has a decomposition temperature which is relatively low) in order to obtain a film of relatively large thickness.

To obtain on the flat glass a reflecting power greater than 30% to visible light, it is preferable to use a relatively large quantity of titanium acetylacetonate which gives a high yield on deposition.

In the present invention it is preferable to have in the solution at least 20% by volume of a titanium chelate other than the acetylacetonate to obtain a very strong film having good uniformity.

It is also preferable according to the invention to dissolve the titanium chelates in an organic solvent to a concentration of 5 to 80% by volume. As an organic solvent there may be used many types of polar and non-polar solvents of various densities, viscosities and latent heats of evaporation but it is preferable to choose a solvent having a boiling point greater than 100°C. As solvent there may be mentioned the alcohols (such as normal butyl alcohol, iso-butyl alcohol, and normal amyl alcohol), the ketones (such as methyl-propyl-ketone, methyl-n-butylketone, methyl-n-amylketone), esters (such as n-butyl acetate, isoamyl acetate, iso-propyl acetate), glycol ethers (such as ethylene glycol mono-ethyl-ether, ethylene glycol diethylether, ethylene glycol monobutyl ether), aromatic hydrocarbons (such as toluene, xylene), and compounds having a high boiling point (such as diethylene glycol diethylether, diethylene glycol monobutylether). There may also be used as a solvent in the present invention, ligands formed by molecules entering into the composition of the titanium chelates such as acetyl acetone, methyl acetoacetate, ethyl acetoacetate, octylene glycol and triethanolamine.

In the use of the present invention, the solution containing at least two types of titanium chelate chosen among titanium acetylacetonate, titanium methylacetoacetate, titanium ethylacetoacetate, titanium tetraoctylene glycol and titanium triethanolamine, is atomised or otherwise deposited on the glass surface heated to a high temperature to form a film of titanium oxide. The reason for obtaining a film of excellent uniformity has not yet been discovered but it is believed that the process proceeds in the following manner.

During impact of a molecule of titanium chelate on the surface of glass heated to a high temperature, a chemical bond between the ligand and the titanium is broken and the polymerisation reaction of TiO proceeds at a high speed. For a titanium compound having a low temperature of dec mposition, the greatest part

of a thermal decomposition reaction takes place in a very short interval of time after impact of a droplet on the surface of the glass which leads only to local f r-mation of the film. On the other hand for a titanium compound having a high temperature of decomposition the thermal decomposition reaction starts immediately after impact of the droplets on the surface of the glass but it continues for an appreciable duration of time during which the atomised droplets spread on the surface thus forming a uniform coating film.

On the other hand, for a titanium compound having a high temperature of decomposition, it is considered that a reaction in the gaseous phase takes place at the surface of the glass brought to a high temperature to give a coated film which is denser because such a chelate is not decomposed on the surface of the hot glass but is present in the gaseous phase.

The process of the present invention may be applied to a film of glass formed continuously starting from molten glass. In this process for treatment of glass continuously the solution of titanium compound is pulverised by means of a pulverising device which is displaced transversely to the direction of advance of the glass film brought to a high temperature. In this case the lack of uniformity of the coated film which would appear following displacement of the pulveriser may be eliminated and the portion of the film having a coating of uniform thickness transversely to the ribbon increases so that the usable width of the coating is also increased.

On the other hand, given that in the process of the present invention there is used at least two types of titanium compound which have different characteristics of thermal decomposition the choice of the composition of the solution of titanium compounds ensures constant conditions which are stable for formation of the coated film independently of the thermal conditions of the sheet of glass and its thickness. Further, the use of titanium chelates at a concentration from 5 to 80% by volume in an organic solvent easily leads to the formation of a coated film having good mechanical properties, a large chemical inertness and a uniform thickness. When there is dissolved in the solution a quantity of titanium chelate greater than 80% by volume the viscosity of the solution increases so that pulverisation becomes difficult and the number and dimensions of the titanium oxide particles formed in the coated film increase which can give a defective appearance to the film. Further if there is dissolved less than 5% by volume of the titanium chelate in the solution, a large part of the solvent has the effect of cooling the pre-heated surface of the glass so that the film is then formed at a low temperature. The film obtained may then have mediocre properties (mechanical properties and chemical inertness).

When there is used an organic solvent having a boiling point greater than 100°C the dimensions of the titanium oxide particles formed are generally so small that they are invisible to the naked eye which considerably improves the uniformity of the film. In use of the invention it is possible to add to the solution of titanium chelate a thermally decomposable metal compound to form a coloured metal oxide which allows production starting from the solution, of a coloured film containing titanium oxide and said coloured metal oxide.

Preferred embodiments of the invention will be described in the following Examples. "Reference samples" are given by way of comparison.

EXAMPLE 1.

A solution of titanium chelate was sprayed at the outlet of a furnace for manufacturing flat glass by flotation on a bath of molten metal on to the glass ribbon obtained (dimensions of the glass ribbon 3 m width and 6 mm thickness).

The glass left the furnace at 580°C and was displaced at a speed of 3.2 m per minute. Spraying was carried out under a pressure of 4 kg/cm² with a sprayer which was displaced in to and fro movement perpendicular to the direction of advance of the glass ribbon.

The ribbon coated with a solution forming the titanium oxide film was passed through a re-heating enclosure and after re-cooling it was cut.

The solution of titanium chelate which was pulverised on the glass surface was composed of:

— 30 cm³ of titanium acetylacetonate
— 20 cm³ of tetraoctylene glycol titanate

and

— 50 cm³ of xylene.

By means of this solution there was prepared sample No. 1.

The sample was studied from the point of view of optical properties and the following results were obtained:

— reflection to visible light 33%
— transmission of visible light 64%
— total reflection of solar radiation 25%
— total transmission of solar radiation 62%

In Table 1 there are given the characteristics of resistance of a film to abrasion and also resistance to alkalis and acids. In the last column of the Table there is also given the degree of uniformity of the film.

The abrasion trials were carried out on an abrasion machine (load 600 g/cm², speed of rotation 300 revs. per minute, distance from the point of application of the load to the centre of rotation 70 mm, and surface of application of the load 1 cm², abrasive tissue : 6 layers of gauze impregnated with a polishing agent for glass (GLASTER — registered trade mark). The state of the film is observed after each period of 100 revolutions of the sample and the degree of resistance to abrasion is expressed by the number of revolutions necessary for the film to be very slightly damaged.

The trial for resistance to alkalis is effected by immersing the sample in a normal aqueous solution of caustic soda at 25°C for 10 days and observing each day the appearance of the film.

The trial for resistance to acids is carried out by immersing the sample in a normal aqueous solution of hydrochloric acid at 25°C for 10 days and observing each day the appearance of the film.

The uniformity of the film of the sample is appreciated in the following manner.

The sample of coated glass (dimensions 90 x 60 cm) is placed on a black tissue to provide a background and the appearance of the sample is estimated by visual observation from a distance of 10 metres from the sample.

By way of comparison there was prepared a reference solution containing as a titanium chelate 50 cm³ of titanium acetylacetonate in 50 cm³ of xylene.

The reference sample 1 was prepared in the same manner as sample 1 except that the solution used for forming the film was the reference solution.

The reference sample 1 showed the same optical properties as the sample 1 according to the invention but the reference sample had worse properties regarding resistance to abrasion and alkalis and acids. Further it will be seen that the uniformity of the film of the reference sample 1 was greatly inferior to that of the sample according to the invention.

TABLE 1

Sample	Tests			Uniformity of film
	Abrasion	Resistance to alkali	Resistance to acid	
Reference 1	100/200 revs/min	Torn after 1 day	Damaged after 1 day	Interference colours visible
Reference 2	50/150	Torn after 1 day	Damaged after 1 day	,,
Sample 1	500/800	Unchanged after 10 days	Unchanged after 10 days	Uniform film
,, 2	300/400	,,	,,	,,
,, 3	300/400	,,	,,	,,
,, 4	400/500	,,	,,	,,
,, 5	600/800	,,	,,	,,
,, 6	400/500	,,	,,	,,
,, 7	400/500	,,	,,	,,
,, 8	400/500	,,	,,	,,

EXAMPLE 2.

A sample 2 was prepared using a solution of titanium chelate formed of 35 cm³ of titanium acetylacetonate, 15 cm³ of titanium tetraethanolamine, 25 cm³ of xylene and 25 cm³ of isoamyl acetate, the spraying conditions being the same as in Example 1.

The sample 2 has approximately the same optical characteristics as those of sample 1 and it has a mechanical and chemical resistance and also a uniformity of film greater than those of the reference sample 1 as will be seen in Table 1.

EXAMPLE 3.

A sample 3 was prepared using a solution of titanium chelate formed of 30 cm³ of titanium methyl acetoacetate 20 cm³ of titanium tetraoctylene glycol and 50 cm³ of xylene. The spraying conditions are the same as in Example 1.

The sample 3 has approximately the same optical characteristics as the sample 1 and it has properties of mechanical strength and chemical inertness and uniformity of film superior to those of reference sample 1 as will be seen in Table 1.

EXAMPLE 4.

The sample 4 is obtained using a solution of titanium chelate formed of 35 cm³ of titanium ethylacetoacetate, 15 cm³ of titanium tetraoctylene glycol and 50 cm³ of xylene. The spraying conditions are the same as in Example 1.

The sample 4 has approximately the same optical characteristics as those of sample 1 and it has properties of mechanical strength, chemical inertness and film uniformity superior to those of the sample of reference 1 as seen in Table 1.

EXAMPLE 5.

The sample 5 is prepared using a solution of titanium chelate compound of 15 cm³ of titanium acetylacetonate, 15 cm³ of titanium ethyl acetoacetate, 20 cm³ of titanium tetraoctylene glycol and as solvent a mixture of 25 cm³ of xylene and 25 cm³ of butanol.

The spraying conditions are the same as in Example 1.

The sample 5 has approximately the same optical characteristics as those of sample 1 and it has properties of mechanical strength, chemical inertness and film uniformity which are superior to those of reference sample 1 as seen in Table 1.

EXAMPLE 6.

The sample 6 is prepared using a titanium chelate solution formed of 25 cm³ of titanium acetylacetonate, 25 cm³ of titanium ethyl acetoacetate and 50 cm³ of xylene.

The spraying conditions are the same as in Example 1.

The sample 6 has the same optical characteristics as those of sample 1 and it has properties of mechanical strength, chemical inertness and film uniformity superior to those of reference sample 1 as seen in Table 1.

EXAMPLE 7.

The sample 7 is prepared using a solution of titanium chelate formed of 15 cm³ of titanium methyl acetoacetate, 20 cm³ of titanium ethylacetoacetate and 65 cm³ of xylene. The spraying conditions are the same as in Example 1.

The sample 7 has approximately the same optical characteristics as those of sample 1 and it has properties of mechanical strength, chemical inertness and film uniformity superior to those of reference sample 1 as seen in Table 1.

EXAMPLE 8.

At the output of a chamber for manufacture of glass floating on a bath of molten metal, there is sprayed a solution of titanium chelates on a glass ribbon of which the dimensions are about 3 m width and 10 mm thickness. The glass ribbon is heated at 580°C and is displaced at a speed of 3.2 metres per minute. Spraying is carried out at a pressure of 4 kg/cm² by means of a sprayer which is displaced in to and fro movement transversely to the direction of advance of the glass ribbon; the surface of the glass is covered with a solution which forms a titanium oxide film, the ribbon then being passed in a re-heating enclosure and cut up after cooling.

The solution of titanium chelate which is pulverised on the surface of the glass is formed of 30 cm³ of titanium acetylacetonate, 15 cm³ of titanium tetraoctylene glycol and 55 cm³ of xylene as a solvent.

A sample 8 is prepared. The optical characteristics of this sample are approximately the same as those of sample 1. The properties of mechanical strength, chemical inertness and uniformity of film are also indicated in Table 1.

By way of comparison there is prepared a reference sample 2 using the same conditions of spraying as in Example 8, but using as the solution of titanium chelate a mixture f 50 cm^3 of titanium acetylacetonate and 50 cm^3 of xylene as solvent. The reference sample 2 has the same optical characteristics as those of sample 2 but the reference sample 2 gives inferior results regarding the mechanical strength and chemical inertness and also uniformity of film in comparison with sample 8 as appears from Table 1.

After the preceding trails, it is apparent that the glass coated with a film of titanium oxide according to the method of the present invention, has characteristics of mechanical strength, chemical inertness and film uniformity superior to those of the film prepared by the known process.

EXAMPLE 9.

There is placed a sheet of float glass (30 cm x 30 cm x 5 mm) in an electric furnace heated at 670°.

The sample is left for 4 minutes in the furnace and then is removed and there is sprayed on the hot glass plate a solution of titanium chelate described below with a feed of 25 cm^3/mn for 8 to 10 seconds at a pressure of 3 kg/cm^2 using a sprayer (registered trake mark WIDER 60).

There is thus obtained a glass plate covered with a film having a reflective power of about 33% for visible light. Each spraying solution is formed of 30 cm^3 of titanium acetylacetonate, 20 cm^3 of titanium tetraoctylene glycol and 50 cm^3 of one of the organic solvents listed in Table 2.

Each time the appearance of the titanium oxide film thus produced is estimated by examining with the naked eye the particles of titanium oxide in the film and counting the particles by means of a microscope. The appearance of the film thus obtained is thus indicated in Table 2. As will be seen from the Table there is always obtained a film of excellent uniformity if there is used an organic solvent having a boiling point of greater than 100°C.

TABLE 2

Organic solv nt	Boiling P int °C	Appearance f film	
		Number of particles /cm²	Particles bserved by the naked eye
Methylene chloride	40	480	Large number visible
Methanol	65	350	,, ,, ,,
Ethanol	78	330	,, ,, ,,
Benzene	80	360	,, ,, ,,
Isopropyl alcohol	82	170	Visible
N-Heptane	98	126	,,
Toluene	111	40	Invisible
Butanol	118	17	,,
N-Butylacetate	126	16	,,
Ethylene glycol-monomethylether	135	14	,,
Xylene	144	40	,,
Isoamyl acetate	145	12	,,
Diethylene glycol-diethylether	188	26	,,
Xylene-butanol (1:1) mixture	–	36	,,
Xylene-acetate isoamyl (1:1) mixture	–	30	,,

EXAMPLE 10.

There is deposited by a spraying as in Example 9 various solutions of titanium chelates on glass plates which are heated to produce a film of titanium oxide.

Each spraying solution used is formed of 40 cm³ of titanium methylaceto-acetate and 10 cm³ of titanium tetraoctylene glycol dissolved in 50 cm³ of one of the organic solvents mentioned in Table 3.

There is observed each time the appearance of film of titanium oxide and the possible presence of titanium oxide particles in the same way as in Example 9.

The results are indicated in Table 3.

As will be seen, the film has excellent uniformity when the organic solvent used has a boiling point greater than 100°C.

TABLE 3

Organic solvent	Boiling Point °C	Appearance of film: Number of particles /cm²	Appearance of film: Particles observed by the naked ye
Methylene chloride	40	710	Large number visible
Methanol	65	640	,,
Ethanol	78	620	,,
Benzene	80	570	,,
Isopropyl alcohol	82	420	,,
N-Heptane	98	150	Visible
Toluene	111	102	Slightly visible
Butanol	118	30	Invisible
N-Butylacetate	126	15	,,
Ethylene glycol-monomethylether	135	30	,,
Xylene	144	16	,,
Isoamylacetate	145	21	,,
Diethylene glycol-diethylether	188	16	,,
Xylene-butanol (1:1) mixture	–	20	,,
Xylene-acetate isoamyl (1:1) mixture	–	20	,,

EXAMPLE 11.

On glass plates heated in the same conditions as Example 9 there were deposited various solutions of titanium chelates to produce films of titanium oxide. Each spraying solution is formed of 30 cm³ of titanium ethylacetoacetate and 20 cm³ of titanium tetraoctylene glycol dissolved in 50 cm³ of one of the solvents of Table 4. There is observed the appearance of the film and especially the presence of titanium oxide in the same manner as in Example 9. The results are shown in Table 4. As will be seen in the Table there is obtained a film of excellent uniformity when there is used a solvent having a boiling point greater than 100°C.

TABLE 4

Organic solvent	Boiling Point °C	Appearance of film	
		Number of particles /cm²	Particles observed by the naked eye
Methylene chloride	40	470	Large number visible
Methanol	65	450	,,
Ethanol	78	470	,,
Benzene	80	420	,,
Isopropyl alcohol	82	320	,,
N-Heptane	98	130	Visible
Toluene	111	90	Hardly visible
Butanol	118	46	Invisible
N-Butylacetate	126	26	,,
Ethylene glycol-monomethylether	135	8	,,
Xylene	144	29	,,
Isoamyl acetate	145	32	,,
Diethylene glycol-diethylether	188	12	,,
Xylene-butanol (1:1) mixture	–	19	,,
Xylene-acetate isoamyl (1:1) mixture	–	18	,,

EXAMPLE 12.

There are applied onto glass plates heated by the same spraying process as in Example 9 various solutions of titanium chelate in such a manner as to produce on the glass a film of titanium oxide. Each solution used is formed of 20 cm³ titanium acetylacetonate, 10 cm³ of titanium ethylacetoacetate, 20 cm³ of titanium tetraoctyleneglycol and 50 cm³ of one of the organic solvents mentioned in Table 5.

The appearance of the film and possible presence of titanium oxide particles are observed by the same method as in Example 9.

The results are indicated in Table 5. As will be seen from this Table there is obtained a film of excellent uniformity when the solvent is an organic solvent having a boiling point greater than 100°C.

TABLE 5

Organic solvent	Boiling P int °C	Appearance of film	
		Number f particles /cm²	Particles bserved by the naked eye
Methylene chloride	40	400	Large number visible
Methanol	65	420	,,
Ethanol	78	310	,,
Benzene	80	320	,,
Isopropyl alcohol	82	110	Visible
N-Heptane	98	95	,,
Toluene	111	70	Hardly visible
Butanol	118	40	Invisible
N-Butylacetate	126	40	,,
Ethylene glycol-monomethylether	135	36	,,
Xylene	144	26	,,
Isoamyl acetate	145	35	,,
Diethylene glycol-diethylether	188	28	,,
Xylene-butanol (1:1) mixture	–	36	,,
Xylene-acetate isoamyl (1:1) mixture	–	36	,,

EXAMPLE 13.

On glass plates which are heated there is sprayed by the process of Example 9 various solutions of titanium chelate in order to produce a film of titanium oxide on the glass. Each spraying solution used is formed of 30 cm³ titanium acetylacetonate, 20 cm³ of tetraoctylene glycol titanium, 3 grams of iron acetylacetonate, 3 grams of chromium acetylacetonate and 50 cm³ of one of the solvents of Table 6. The properties of the film and the possible presence of titanium oxide particles are observed in the same way as in Example 9. The results are indicated in Table 6 in which it is possible to see that the film has excellent properties of uniformity when the solvent used has a boiling point greater than 100°C.

TABLE 6

Organic s lvent	Boiling Point °C	Appearance of film	
		Number of particles /cm²	Particles observed by the naked eye
Methylene chloride	40	520	Large number visible
Methanol	65	450	,,
Ethanol	78	430	,,
Benzene	80	410	,,
Isopropyl alcohol	82	220	,,
N-Heptane	98	120	Visible
Toluene	111	93	Hardly visible
Butanol	118	20	,,
N-Butylacetate	126	36	,,
Ethylene glycol-monomethylether	135	14	,,
Xylene	144	36	,,
Isoamyl acetate	145	27	,,
Diethylene-glycol diethylether	188	8	,,
Xylene-butanol (1:1) mixture	–	19	,,
Xylene-acetate isoamyl (1:1) mixture	–	8	,,

As will appear from the description above, owing to the process of the invention, there is avoided the adhesion of titanium oxide particles on the coating film and there is no alteration in the good appearance of the film of titanium oxide.

WHAT WE CLAIM IS:—

1. A method of applying a coating comprising titanium oxide to a glass surface, in which a solution containing at least two titanium compounds selected from titanium acetylacetonate, titanium methyl acetoacetate, titanium ethyl acetoacetate, titanium tetraoctylene glycol and titanium triethanolamine is applied to the surface which is at an elevated temperature sufficient to decompose the compounds to titanium oxide.

2. A method according to Claim 1, in which the solution comprises an organic solvent having a boiling point of at least 100°C.

3. A method according to either preceding claim, in which the temperature of the surface is from 500° to 700°C.

4. A method according to any preceding claim, in which the solution is sprayed on to the surface.

5. A method according to Claim 4, in which the solution is sprayed on to a surface of a ribbon of glass prepared by the float glass pr cess.

6. A method according to any preceding claim, in which the solution contains from 5 to 80% by volume of said titanium compounds.

7. A method according to any preceding claim, in which the solution contains at least 20% by volume of said titanium compounds other than titanium acetylacetonate.

8. A method according to any preceding claim, in which the solution contains a compound of a metal other than titanium capable of forming an oxide of said metal on heating.

9. A method of applying a coating comprising titanium oxide to a glass surface, substantially as hereinbefore described with reference to the Examples.

10. Glass articles provided with a titanium oxide coating applied by a method according to any preceding claim.

For the Applicants,
RAWORTH, MOSS & COOK,
Chartered Patent Agents,
36 Sydenham Road,
Croydon, Surrey.
— and —
75 Victoria Street,
Westminster,
London, S.W.1.

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